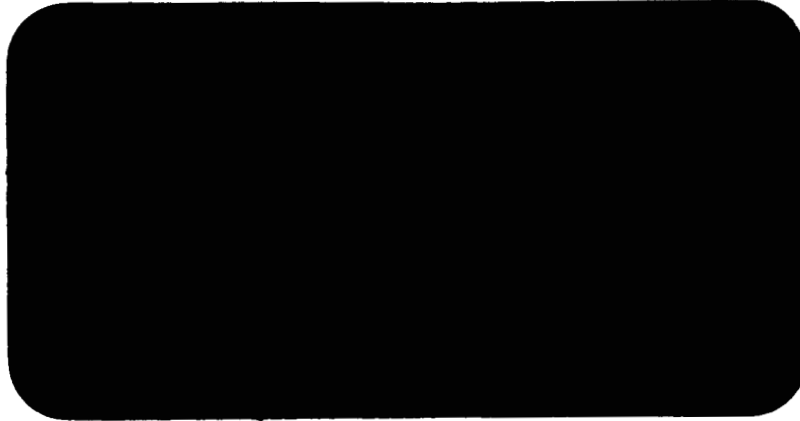


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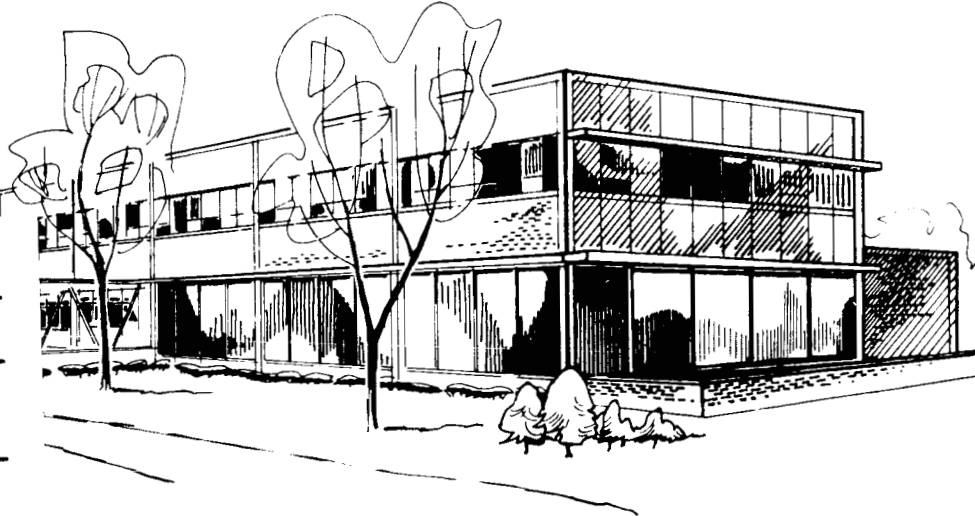


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DEVELOPMENT OF CHEMICAL ANALYSIS TECHNIQUES
FOR

ADVANCED MATERIALS RESEARCH PROGRAM

(Second Quarterly Progress Report)

covering the period
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Prepared for: Jet Propulsion Laboratory
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Development of Chemical Analysis Techniques
for
Advanced Materials Research Program

I. SUMMARY

The past three months of this study, aimed at the development of reliable analytical techniques, have been devoted almost exclusively to mass-spectrographic analysis. After an extensive literature survey in the first quarter, a joint decision was reached by JPL and SRRC personnel to employ spark-source mass spectrography for JPL problems wherever possible.

The use of mass spectrography for impurity analysis in metal systems is a well-accepted technique. However, this technique has not been widely used for the analysis of nonconductors, such as MgO , or for the analysis of gases, of which two applications would be fruitful if they could be brought to bear on JPL materials. Thus, a great deal of effort has been expended during this period in an attempt to use the mass spectrograph for these two purposes.

In order to evaluate the effectiveness of these procedures, we have been using standard samples and techniques to check mass-spectrograph results. We have been unable to find standard refractory oxide materials which are certified for gas content, but we have been able to obtain metal standards from NBS which contain known amounts of nitrogen, oxygen, and carbon. These have been run successfully.

The emission spectrograph is being used as a check method for impurity analyses. Preliminary results here indicate that standard arc techniques will not give reliable results at the low sensitivity required

for some impurity analyses. The major impurities, such as calcium and aluminum, have given good checks on mass-spectrograph results, but elements present in the 1-20 ppm range will require a more refined technique. In order to obtain better sensitivity and reasonable accuracy, we will try to use a solution technique for impurities present at low concentration.

The one analysis which apparently cannot be handled satisfactorily by the mass spectrograph is that for hydrogen. We have made numerous attempts to analyze both metals and nonconductors for hydrogen content, but the results do not appear reliable. The most probable cause of trouble here is in the instrument itself. The magnet pole pieces and the electrostatic sectors are massive steel which have been fired in hydrogen. This leads to a persistently high hydrogen background — over 600-800 ppm as compared to about 1 ppm for oxygen or nitrogen. However, there is a rapid and reliable method for hydrogen which we will use (hot-extraction technique), which will be more fully described in the next section.

Details of the problems mentioned above are given in the next section.

II. ACTIVITY DURING THE REPORTING PERIOD

A. Analysis of Interstitials

The analytical conditions for the determination of carbon, nitrogen, and oxygen by mass spectrography have been determined, and we are now analyzing these elements routinely.

Experimental work on the development of this technique has been divided into three parts: first, the effects of etching; second, baking; and third, an evaluation of the instrument blank level.

1. The most obvious source of extraneous nitrogen, oxygen, or carbon is surface contamination of the sample. If the sample has been handled, cut with tools, or packaged in improper containers, this history will be clearly shown in the analysis. Therefore, some cleaning procedure which will remove these contaminated surface layers is indicated. Chemical etching and electrical cleaning are the most commonly used methods. Unfortunately, the geometry of the source area of the mass spectrograph prohibits the use of ion or electron bombardment cleaning unless extensive modifications are made. Experience of other laboratories, where the modifications necessary for the installation of ion bombardment cleaning have been made, indicates that the method is unsatisfactory even with another provision for rotation of the sample.

Chemical etching was investigated and has proved quite satisfactory. High-purity "Transist AR"-grade acids were used throughout these experiments and all etching was done in Teflon beakers to reduce contamination from leaching of glass beakers.

At first it was feared that any oxidizing acid, such as HNO_3 , would be unsuitable because of the formation of surface oxide layers. However, we have been able to avoid this difficulty by extensive presparking of the samples. To evaluate this problem, two steel samples (NBS 1042 and 1045) were etched in HNO_3 and then run on the mass spectrograph with varying lengths of presparking. It was found that a 3×10^{-8} coulomb exposure cleans away any oxide layer and allows analysis of the bulk material.

Experiments using HF , HCl , and H_2SO_4 were also performed and similar results were obtained. A prespark exposure of from 3×10^{-8} to

1×10^{-7} coulombs was adequate in all cases to allow analysis of interstitials in the bulk of the sample.

2. Baking of the sample after it has been placed in the source is necessary because the walls of the source can contribute material to interfere with these analyses.

Normal baking of the MS-7 source is a somewhat questionable procedure since it exposes the sample and the source to oil from the diffusion and rough pumps. The physical arrangement of the pumping system allows the vapor from the pumps free access to the source. However, the Sperry MS-7 is ion-pumped and we have a much smaller background than oil-pumped systems. Baking reduces the contribution from material adsorbed on the sample during etching and rinsing, as well as making a major reduction in interferences from the walls of the source chamber.

The procedure for evaluating the effectiveness of the baking step was similar to that used for etching procedures. Samples were etched and loaded into the instrument. The most economical method was to load a fresh sample in the late afternoon and bake for twelve hours, after which a timer cut off power to the heating bands. In this manner, the source was cool enough to run in the morning.

Baking temperatures were obtained by placing a maximum reading thermometer in the source prior to baking and reading the maximum temperature after the sample had been run. The highest baking temperature we have used so far is 200°C . It is not likely that we can increase this to much over 250°C .

3. Evaluation of the instrument blank level is difficult, but we have been able to make an educated guess by running some inert materials.

Gold was analyzed extensively for nitrogen and oxygen, since this material seemed to be least likely to form an oxide or nitride or to contain any significant amounts of dissolved gas. This apparently is true for oxygen and only slightly less true for nitrogen. The average apparent oxygen value for a series of four runs was 0.7 ppm atomic. The corresponding nitrogen value was 1.0 ppm atomic. We have not seen any values lower than 0.3 ppma for oxygen and 0.8 ppma for nitrogen. These may represent values for the metal itself and certain material, such as CdS, may indeed show a much smaller gas blank.

The technique we have evolved for analyzing interstitials is as follows: First, the sample is etched in high-purity, strong acid, sufficient to remove appreciable material from the surface, followed by copious rinsing in distilled water. It is then placed in the mass spectrograph while still wet, pumped, and baked at 200°C, for at least twelve hours. Then a long, prespark exposure (3×10^{-8} to 1×10^{-7} coulombs) is made to remove adherent oxide and adsorbed gases. Finally, the analytical exposures are taken in reverse order, that is, the longest exposures are taken first. Studies at Battelle and G. E. Research Laboratory indicate that if a sample is heated and then cooled in the mass-spectrograph source it will re-adsorb appreciable quantities of gas. By keeping the sample hot with a long pre-spark exposure and then doing the longest analytical exposure first, followed by shorter exposures, this tendency to re-adsorption is kept to a minimum.

The gases which are evolved from the source chamber have been examined in several laboratories with partial pressure analyzers. These residual gases have been identified as hydrogen, methane, water vapor, nitrogen, carbon monoxide, and carbon dioxide. Attempts to remove or reduce

the level of these gases met with failure. Apparently there is a source of these gases within the instrument.

The results of our standardization with NBS materials are shown below. Also included are the results of oxygen analyses on an AEC zircaloy standard.

Table 1. Gas analyses on standard materials.

| | | <u>ppm(weight)</u> | | | |
|--------------|------|--------------------|-------------------------|-----------------|---------------------------|
| | | <u>Oxygen</u> | <u>Oxygen found</u> | <u>Nitrogen</u> | <u>Nitrogen found</u> |
| NBS 1042 | 170 | | 240 | 140 | 250 |
| | | | 200 | | 200 |
| | | | 160 | | 250 |
| | | | 310 | | 150 |
| | | | 330 | | 180 |
| | | | 160 | | 110 |
| | | | average | | 190 |
| | | | | | |
| NBS 1045 | 70 | | 140 | 40 | 35 |
| | | | 110 | | 60 |
| | | | 90 | | 50 |
| | | | 135 | | 55 |
| | | | 80 | | 35 |
| | | | 115 | | 45 |
| | | | average | | 47 |
| | | | | | |
| K18 zircaloy | 1120 | | 1250 | | |
| | | | 1050 | | |
| | | | 980 | | |
| | | | 900 | | |
| | | | 900 | | |
| | | | 880 | | |
| | | | average | | 990 |
| | | | | | |

The accuracy and precision of these analyses appear quite acceptable.

Each of these materials has been checked for oxygen content by inert gas fusion and good agreement with the accepted value has been obtained.

The effect of various etchants on the carbon analysis is negligible. Two high-alloy NBS steel samples were investigated with the results shown in Table 2.

Table 2, Carbon analysis by mass spectrography.
(ppm weight)

| | <u>C</u> | <u>C found</u> |
|-----------|----------|----------------|
| NBS 101 e | 540 | 710 |
| | | 600 |
| | | 590 |
| | | 620 |
| | | 590 |
| | | average 620 |
| NBS 1042 | 1000 | 1200 |
| | | 1200 |
| | | 1350 |
| | | 1400 |
| | | 1250 |
| | | average 1300 |

Baking and presparking were used, as in nitrogen and oxygen analyses, and no effects were seen with variations in the etchant.

B. Impurity Analyses

Impurity analyses are being performed on two batches of MgO powder and a group of compacts which have been prepared by pressing the two powdered materials. We have had some unexpected difficulties with the results of these analyses, and we are trying to find the reasons for these problems.

Briefly, good checks were obtained with one batch of powder (M-300) but the other powder (JPL-8) appears to have a higher impurity content. Table 3 shows the results of the first analyses on these powders which were obtained by mixing with pure silver powder and pressing to form electrodes.

The high value for fluorine seen in the JPL #8 sample may be attributed to the fact that this analysis was performed on an unbaked sample. There is a large difference (up to a factor of 100 in some cases)

in the apparent concentration of certain impurities before and after baking. Peaks which show this effect include F^+ (19), OH^+ (17), H_2O^+ (18), and Cl^+ (35 and 37). The effects of baking on the height of these peaks is quite striking. The fluorine peak in JPL #8 is successively reduced by baking until it levels off at 180 ppma. Baking at $200^{\circ}C$ is sufficient to reduce these volatile impurities to a minimum.

Table 3. Analytical results on powdered MgO .
(ppm atomic)

| | <u>JPL #8</u> | <u>Fisher M-300</u> |
|----|---------------|---------------------|
| B | < 1 | 3 |
| N | no value | 90 |
| F | 3000 | 100 |
| Na | < 3 | 90 |
| Al | 470 | 85 |
| Si | 1700 | 2800 |
| P | 38 | 110 |
| S | 360 | 520 |
| Cl | 570 | 310 |
| K | 60 | - |
| Ca | 150 | 150 |
| Ti | - | 13 |
| Cr | 2* | 5* |
| Mn | 2* | 3* |
| Fe | 45 | 100 |
| Ni | 10 | 10 |
| Co | 12 | 13 |
| Zn | 15 | 15 |

* Probable die contamination

The original MgO -silver compact has been re-examined several times with and without baking and the results are consistent and some reduction of the volatile impurities is noted after baking. Apparently this particular compact picked up higher impurity levels from the die than we normally anticipate. We have made several new compacts with this sample and it is being analyzed again. Preliminary results indicate that

at least some of the values previously reported are in error. For example, the aluminum content in the new compacts is about 30 ppm by weight, and we have an excellent check by emission spectroscopy which gives a value of 50 ppm. These analyses will be completed shortly.

Two problems have arisen in the analysis of the MgO compacts. Using the technique reported by Socha and Leipold for insulating powders, one difficulty lies in the uncontrolled amount of gold from the counter electrode appearing in the spectrum. A private communication from A. J. Socha stated that he had been able to limit the gold to 5% of the total ion current. This would be ideal and we are trying to duplicate this work.

The second problem which we have encountered is concerned with a large hydrocarbon impurity in the compacted samples. This may be due to the plastic vials which hold the samples. We have seen hydrocarbons with masses 200 and above whose presence makes plate interpretation extremely complex. Severe baking reduces these lines but several baking cycles are necessary and time consuming. New samples packaged in glass have been requested.

In general, it appears that any analysis in which a foreign material is included will be open to question. We have now seen this in MgO-silver compacts, pressed MgO-gold analyses, and also in niobium analyses where the samples were mounted in aluminum holders. In all these cases the metal is of high purity, but since it is difficult to control the amount of foreign metal which appears in the spectrum, it is difficult to separate the impurities in the sample from the impurities in the metal. It is also possible for holders or counterelectrodes to heat

up and emit thermal ions such as sodium, potassium, and calcium.

The ideal solution would be to draw a spark between two pieces of MgO. We have had success with this technique on CaWO_4 and it may be worth trying with MgO. If very high spark voltages are used, the electrodes become incandescent and then a spark is initiated. After the spark has started it is possible to reduce the spark voltage to a reasonable value. The key to the spark initiation may be volatilization or decomposition of the sample. We will try the technique in the near future.

C. Mass Spectrographic Check Analyses

We have been concentrating on an emission spectrographic method to check mass-spectrographic impurity analyses. First attempts at emission analyses revealed that standard arc techniques will not give sufficient sensitivity to check impurities in the 1-20 ppm range. We have confirmations on the level of such elements as iron, calcium, and aluminum, as shown in Table 4. These checks are in good agreement principally because the emission method has adequate sensitivity for these particular elements. On the other hand, our present procedure seems totally inadequate for silicon. Examination of several plates would indicate a silicon concentration of well under 1 ppm by weight. The mass spectrograph analyses show appreciable quantities of silicon (~ 100 ppm), so it is obvious that the silicon is not being excited in the dc arc. The cause of this type of error appears to be in the relatively cool arc which results from the burning MgO. Sufficient temperatures to excite the silicon are not generated and another technique is indicated.

Table 4. Comparison of mass and emission spectrographic results for certain elements in MgO

| Sample | OP125 | Mass (ppm wt.) | Emission (ppm wt.) |
|--------|-------|----------------|--------------------|
| | Al | 30 | 50 |
| | Ca | 110 | 85 |
| | Fe | 6 | < 10 |
| | Cu | 13 | 10 |
| | OP141 | | |
| | Al | 20 | 50 |
| | Ca | 70 | 90 |
| | Fe | 3 | < 10 |
| | Cu | 15 | 10 |

We are starting to evaluate a solution method for emission analyses which should solve our problems in this area. These problems have included inadequate sensitivity and enhancement of the magnesium lines which preclude their use as internal standards. The method we are evaluating is a graphite spark method developed by Morris and Pink (ASTM Special Technical Publication No. 221) which has excellent sensitivity. The method was originally developed for impurities in semiconductors and seems easily adaptable to MgO. Internal standards may be added directly to the solution and this will solve our other problem.

The procedure involves dissolution of the sample in acid which has been previously analyzed for impurities. An internal standard is added (probably molybdenum) and the solution is then dried on a graphite electrode. The electrode is sparked with a low-energy spark and the spectrum is recorded in the normal manner. We feel confident that this technique will solve our sensitivity problems for emission analyses.

Several checks on the oxygen content of the NBS gas standards have been made by the inert gas fusion technique. Since this material has been extensively analyzed by NBS, by a variety of methods, we did not feel that any great effort should be expended on this aspect of the problem. However, we have made two checks on each of the samples, and we are in excellent agreement. Our answers were within 25% of the stated values.

D. Hydrogen Analysis

A hot-extraction vacuum system has been constructed for the determination of hydrogen. At present the design calls for heating of a sample and collection of the gas driven off. This gas will then be transferred to a known volume and the pressure measured to determine the amount of hydrogen in the sample. We plan to add a section which will contain hot copper to convert any water vapor present to hydrogen. Since the method involves heating the sample in a static vacuum, the system must be leak-tight. Any air leakage during the analysis will lead to erroneously high values. We have encountered some difficulty in reducing the leak-rate of the system. A number of large leaks were encountered when the system was first built. At present we are trying to locate one or two smaller leaks.

III. PLANS FOR NEXT QUARTER

Plans for the next quarter involve a continuation of our effort to clear up problems relating to the analysis of MgO, both as powder and as pressed compacts. Contamination from both the binder and the die will be investigated in the case of JPL #8 MgO. A quantity of high-purity gold wire is available for use as a counter electrode in these analyses.

We will also evaluate the solution technique of Morris and Pink for emission spectrographic analysis for trace impurities in MgO powders. This method should give us the required sensitivity and accuracy.

The hot-extraction hydrogen system will be leak checked and we should have analytical data from this system shortly.

IV OTHER ACTIVITIES

A trip was made to St. Louis to attend the ASTM meeting on mass spectrography. We were able to talk to Mr. A. J. Socha of Bell and Howell in regard to his method for analyzing nonconducting powder compacts. We also took part in a panel discussion concerning the analysis of gases by spark-source instruments.

A series of niobium and copper analyses were also performed during this period and the results are appended.

MRC - ANN

| <u>Nb</u> | |
|-----------|---------------|
| B - | 90 |
| F - | 880 |
| Na - | 320 |
| Mg - | 2700 |
| Al - | holder mat'l. |
| Si - | 8000 |
| Cl - | 1200 |
| K - | 1800 |
| Ca - | 600 |
| Fe - | 820 |
| Cu - | 60 |
| Mo - | 14 |
| Ta - | 11 |
| H - | 1200 |
| C - | 210 |
| N - | 8 |
| O - | 170 |

MRC - UA

| <u>Nb</u> | |
|-----------|------|
| B - | 1 |
| F - | 5 |
| Mg - | 3 |
| Al - | 290 |
| Si - | 350 |
| S - | 5 |
| Cl - | 7 |
| K - | 2 |
| Ca - | 130 |
| Cr - | 3 |
| Fe - | 30 |
| Zr - | 60 |
| Mo - | 15 |
| Ta - | 35 |
| H - | 3800 |
| C - | 480 |
| N - | 5 |
| O - | 19 |

157 - 69

| <u>Cu</u> | |
|-----------|----------|
| Al - | 1 |
| Si - | 7 |
| P - | < 1 |
| S - | < 1 |
| Cl - | 1 etch ? |
| K - | 1 |
| Fe - | 2 |
| Ag - | 2 |
| C - | 75 |
| N - | 10 |
| O - | 15 |

157 - 72

| <u>Cu</u> | |
|-----------|---------|
| B - | 5 |
| F - | 5 etch |
| Mg - | 3 |
| Al - | 10 |
| Si - | 30 |
| P - | 3 |
| S - | 5 |
| Cl - | 15 etch |
| K - | 8 |
| Ca - | 20 |
| Fe - | 10 |
| Ag - | 18 |
| C - | 110 |
| N - | 75 |
| O - | 95 |

157 - 73

| <u>Cu</u> | |
|-----------|----|
| Al - | 25 |
| Si - | 30 |
| Fe - | 1 |
| Ag - | 1 |
| C - | 90 |
| N - | 5 |
| O - | 12 |

157 - 74

| <u>Cu</u> | |
|-----------|-------------------------|
| Si - | 10 |
| Fe - | 8 |
| Ga - | possible at ~ 2 ppma |
| Ag - | 20 |
| C - | 25 |
| N - | 5 |
| O - | 30 |

157 - 77

| <u>Cu</u> | |
|-----------|-------------|
| B - | 1 |
| F - | 300 etch |
| Na - | 1.5 |
| Al - | 2 |
| Cl - | 1100 etch ? |
| K - | 6 |
| Si - | 10 |
| C - | 70 |
| N - | 10 |
| O - | 30 |